Workshop

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Workshop on Advanced Application of Aberration Corrected TEM

像差修正電子顯微學之先進應用研討會

主辦單位

國家同步輻射研究中心 (NSRRC)

國立清華大學工程與系統科學系 (NTHU)

中央研究院物理所 (IOP，AC)

國立台灣大學凝態中心 (NTU)

國立台灣大學尖端奈米材料中心 (NTU)

國立成功大學材料系 (NCKU)

國立交通大學材料系 (NCTU)

國立中山大學材料與光電科學學系 (NSYSU)

工業技術研究院 (ITRI)

中華民國顯微鏡學會 (MSROC)

贊助廠商

FEI Company

JEOL Ltd.

會議議程

11/22

Arrival and Check-in

18:00pm	Reception (Invited speakers and Section Chairman)

11/23

8:30-9:00am	Registration
9:00-9:30am	Opening Keng S. Liang (director of NSRRC) Sunshine Chen (director of Condensed Matter Center)
	Atomic Resolution Spectroscopy Section Chairman: Dr. Di-Jing Huang, NSRRC,
9:30am-10:00am	Christian Colliex Multi-dimensional and multi-signal approaches in (aberration-corrected) scanning transmission electron microscopes
10:00am-10:30am	John Silcox Atomic-scale Chemical Imaging with the NION 'UltraSTEM'
10:30am-10:45am	Coffee Break
10:45am-11:15am	K. Suenaga Single atom imaging and spectroscopy by means of low voltage TEM/STEM with the DELTA corrector
11:15am-11:45am	Yuichi Ikuhara Aberration-Corrected STEM Characterization of Ceramic Interface
11:45am-12:15am	Koji Kimoto High spatial-resolution analysis using STEM-EELS and ADF imaging: Limit of incoherent imaging approximation

12:15am-12:30pm	Min-Wen Chu Preliminary Results on Aberration-Corrected STEM in National Taiwan University: Practical Aspects on STEM-EDX Mapping at Atomic Resolution
12:30am-12:45pm	Photo Taken
12:45pm-14:00pm	Lunch
	Dynamic and In-situ TEM Section Chairman: Professor Jia-Seng Chang, Institute of Physics, Academic Sinica
14:00pm-14:30pm	Nigel D. Browning Dynamic transmission electron microscopy (DTEM)
14:30pm-15:00pm	Kazuo Furuya Ultra-high vacuum electron microscopy and the development of Cs Corrector
15:00pm-15:30pm	Sang Ho Oh Growth and defects dynamics in nano-sized materials studied by transmission electron microscopy
15:30pm-16:00pm	Coffee Break
	Development of Advanced Instrumentation Section Chairman: Professor Liuwen Chang, National Sun Yat-Sen University
16:00pm-16:30pm	Eric Van Cappellen (FEI)
16:30pm-17:00pm	Kondo (JEOL)
18:00pm	Dinner

11/24

Sub-Å Resolution and 3D Structure Quantification

Section Chairman:

Professor Chuan-Pu Liu, National Chen Kung University

Professor Li Chang, National Chiao-Tong University

8:30am-9:00am	Christian Kisielowski Meeting Feynman's challenge
9:00am-9:30am	Kunio Takayanagi 50pm resolution electron microscope, performance and applications
9:30am-10:00am	Les Allen Atomic resolution scanning transmission electron microscopy
10:00am-10:30am	Dirk Van Dyck Processing HREM images to quantitative 3D atomic structures: Where are we?
10:30am-10:45am	Coffee Break
10:45m-11:15am	Angus Kirkland Structural studies of nanoparticles in two and three dimensions using aberration corrected electron microscopy
11:15am-11:45am	Yimei Zhu Atomic imaging and interpretation using secondary electrons and transmitted electrons with an aberration corrected scanning electron microscope

Aberration Free Electron Diffractive Imaging

Section Chairman:

Professor T. K. Lee, Institute of Physics, Academic Sinica

11:45am-12:15am	Jian-Min Zuo Electron Diffractive Imaging at Sub-Å Resolution
12:15pm-12:45pm	Roman Dronyak Three-dimensional electron CDI of a nanocrystal
13:00pm	Lunch
After Lunch	NSRRC Lab Tour http://nanyuan.theonestyle.com/in4.asp

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Multi-dimensional and multi-signal approaches in (aberration-corrected) scanning transmission electron microscopes

C. COLLIEX*, L. BOCHER, N. BRUN, A. GLOTER, D. IMHOFF, M. KOCIAK, K. MARCH, C. MORY, F. de la PENA, O. STÉPHAN, M. TENCÉ, M. WALLS, L. ZAGONEL

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Developments in instrumentation are essential to open new fields of science. This clearly applies to electron microscopy, where recent progress in all hardware components and in digitally assisted data acquisition and processing have radically extended the domains of applications. They provide access to increased performance, to upgraded accuracy and precision and also to unconventional domains lying out of the main stream.

Our purpose will be to demonstrate their impact of these developments within the context of multi-dimensional microscopy (EELS spectrum-imaging), encompassing the spatial as well as the spectral dimensions. Typically, it intimately combines an electron spectroscopy over a very broad spectral domain (from 1 eV up to a few thousands of eV) with high spectral resolution (typically 0.2 to 0.5 eV), and an imaging microscopy with unique spatial resolution, down to a subangström level with an aberration corrected probe forming lens.

Atomic-scale maps of the elemental composition and of the bonding states can now be recorded across hetero-interfaces in artificially grown heterogeneous perovskite-based systems for applications in electronics and spintronics. Some examples in this domain will be shown and discussed. The abruptness of the interfaces at the atomic-scale is demonstrated, along with some analysis of the oxidation states of the metal ions, as it can be deduced from the spatial variations of the fine EELS structures on characteristic core-edges (ELNES).

In the low energy-loss part of an EELS spectrum, the improvement of energy resolution (using a monochromator or deconvolution techniques) allows to measure the local electronic response of the material in terms of band structure (band gap, interband transitions, excitons), and to disentangle it from the long-range response of the neighbouring architecture, encompassing the electromagnetic fields generated by surface and interface plasmons. When applied to individual metallic nanoparticles, the measured EELS signal over the visible spectral domain is closely related to the induced electromagnetic modes, which are governed by the shapes and dimensions of the nanostructures. This technique improves our knowledge of surface plasmon physics and

can assist us in the conception of new structures and devices of interest in

nanophotonics.

Finally, another possibility offered by the introduction of aberration correctors, the gain in free space around the specimen, facilitates the creation of a "nanolaboratory", i.e. a set-up that allows diverse measurements and experiments to be performed in situ.

This work has benefited from the permanent support of CNRS and of fundings (STREP SPANS, Infrastructure ESTEEM) from the European Community.

Atomic-scale Chemical Imaging with the NION 'UltraSTEM'

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In 2008, we reported[1] observations of chemical composition and bonding in a multilayer specimen of $La_{0.7}Sr_{0.3}MnO_3/SrTiO_3$ with a C_3/C_5 aberration-corrected NION UltraSTEM. Color-coded maps of La, Ti and Mn with atomic scale resolution were formed, resulting from observations carried out over a 3.1 nm square image (64x64 pixels) with less than 30 seconds acquisition time. Formation of these images will be discussed as will be the background to the instrument[2]. A key aspect of this instrument is the care taken to control electron trajectories from the specimen to the spectrometer. The result can be the collection of 80 % of the incident electrons - a relatively very high figure. Experience arising from current use of it with magnetic multilayer systems and nanoparticle systems such as CdSe will be outlined. Finally, comments on future directions to be taken with these remarkable tools will be offered.

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Single atom imaging and spectroscopy by means of low voltage TEM/STEM with the DELTA corrector

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Decreasing accelerating voltage of TEM/STEM is sometimes beneficial for single atom imaging and spectroscopy in terms of reduced irradiation damage as well as cross-section increase. An intrinsic difficulty to perform single atom spectroscopy in molecules by means of EELS lies in the electron damage, i.e., the investigated molecules inevitably suffer massive structural damage due to the incident electron probe of high energy[1]. We have therefore employed a newly designed electron optics (the DELTA corrector[2, 3]) so that the accelerating voltage of (S)TEM can be lowered down to 30 - 60kV, which is considerably lower than the carbon knock-on threshold (~ 86 kV) and quite effective to avoid the electron damage for the soft matters.

We will show the successful STEM-EELS analysis at 60kV of the various metallofullerene peapods without the massive electron damages. Single atoms of Ca, La, Ce and Er in the fullerene molecules have been clearly identified. The elemental discrimination of the single atoms with the adjacent atomic numbers has been realized. The measured EELS intensity is only a fraction of the expected one, and finds an important discrepancy in the quantified number of atoms[4].

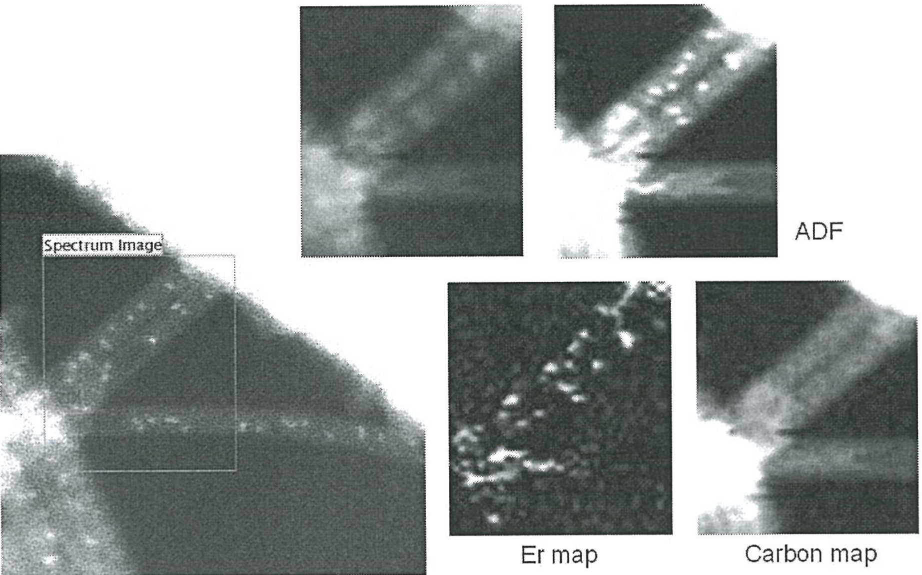

FIG. 1. ADF image of Er@C_{82} peapods and EELS chemical maps for carbon and Er with a constructed color image. Bright dots correspond to the single Er atoms.

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5. This research was supported by JST-CREST project.

Aberration-Corrected STEM Characterization of Ceramic Interface

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Grain boundaries and interfaces of crystals have peculiar electronic structures, caused by the disorder in periodicity, providing the functional properties, which cannot be observed in a perfect crystal. In the vicinity of the grain boundaries and interfaces around the order of 1 nanometer, dopants or impurities are often segregated, and they play a crucial role in the material properties. We call these dopants "function providing elements", which have the characteristics to change the macroscopic properties of the materials drastically.

Z-contrast images obtained by scanning transmission electron microscopy (STEM) is powerful technique to experimentally determine the atomic site of the "function providing elements" segregated at grain boundaries and interfaces. As the image intensity in the Z-contrast is approximately proportional to the square of the atomic number, STEM technique is especially well suited for undestanding the role of heavy impurities in grain boundaries and interfaces composed of much lighter ions. In this paper, the results obtained by Cs (spherical aberration) corrected STEM are demonstrated for well-defined grain boundaries in Al_2O_3 and ZnO bicrystals doped with Y and Pr. In addition, several examples are also demonstrated to characterize the interface structures of $SrTiO_3$ superlattice, $LiFePO_4$ and Au/TiO_2 catalytic system by Cs corrected STEM.

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High spatial-resolution analysis using STEM-EELS and ADF imaging: Limit of incoherent

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Electron energy-loss spectroscopy (EELS) and annular dark-field (ADF) imaging in scanning transmission electron microscopy (STEM) are indispensable tools for material characterization with high spatial resolution. In both methodologies, incoherent imaging model might be firstly assumed, in which an experimental result is a convolution between the probe intensity profile and the object function. Recent experimental results, however, suggest that the convolution model is not exactly valid for high-spatial-resolution domain. In this study, we show our experimental data obtained using STEM-EELS and ADF.

We applied EELS spectrum-imaging scheme[1] for element-selective atomic-column imaging[2]. One of the important factors for realizing high spatial resolution is the optimization of experimental condition to reduce delocalization in inelastic scattering. We demonstrated the effect of delocalization as follows. La atomic columns in $(La,Sr)_3Mn_2O_7$ are observed by using M_5-edge (832eV), but N_{45}-edge (99eV) intensity does not show the clear contrast[2]. Si atomic columns in -Si_3N_4 cannot be visualized using the intensity of Si-L_{23} ELNES (103eV), but are resolved using the intensity at the EXELFS (>300eV)[3]. Delocalization in inelastic scattering means not only the large impact parameter, but inelastically scattered electrons should be considered as partially coherent, which is consistent to recent theoretical investigation[4]. Due to the coherent nature, contrast reversal in inelastic images is observed as well as bright-field (BF) images. Note that BF lattice fringe is preserved through low-loss scattering, and it was reported since the 70's[5, 6].

We applied ADF imaging for crystal structure analysis of $(Tb,Ba)MnO_3$[7] and Eu-doped -SiAlON[8]. Using high signal-to-noise ratio of STEM images, 10-pm atomic displacement can be detected[7]. The accuracy of the atomic position of ADF images depends on the incident probe propagation, which depends on the atomic arrangement around the atomic column of interest. In thick specimen, we have to reexamine the simple incoherent imaging approximation. Even in ADF imaging, specimen thickness should be minimized for intuitive interpretation.

This research is partly supported by JST-CREST and Nano-net by MEXT. We thank Dr. Suenaga, Dr. Findlay, Dr. Shibata and Prof. Ikuhara for invaluable discussions.

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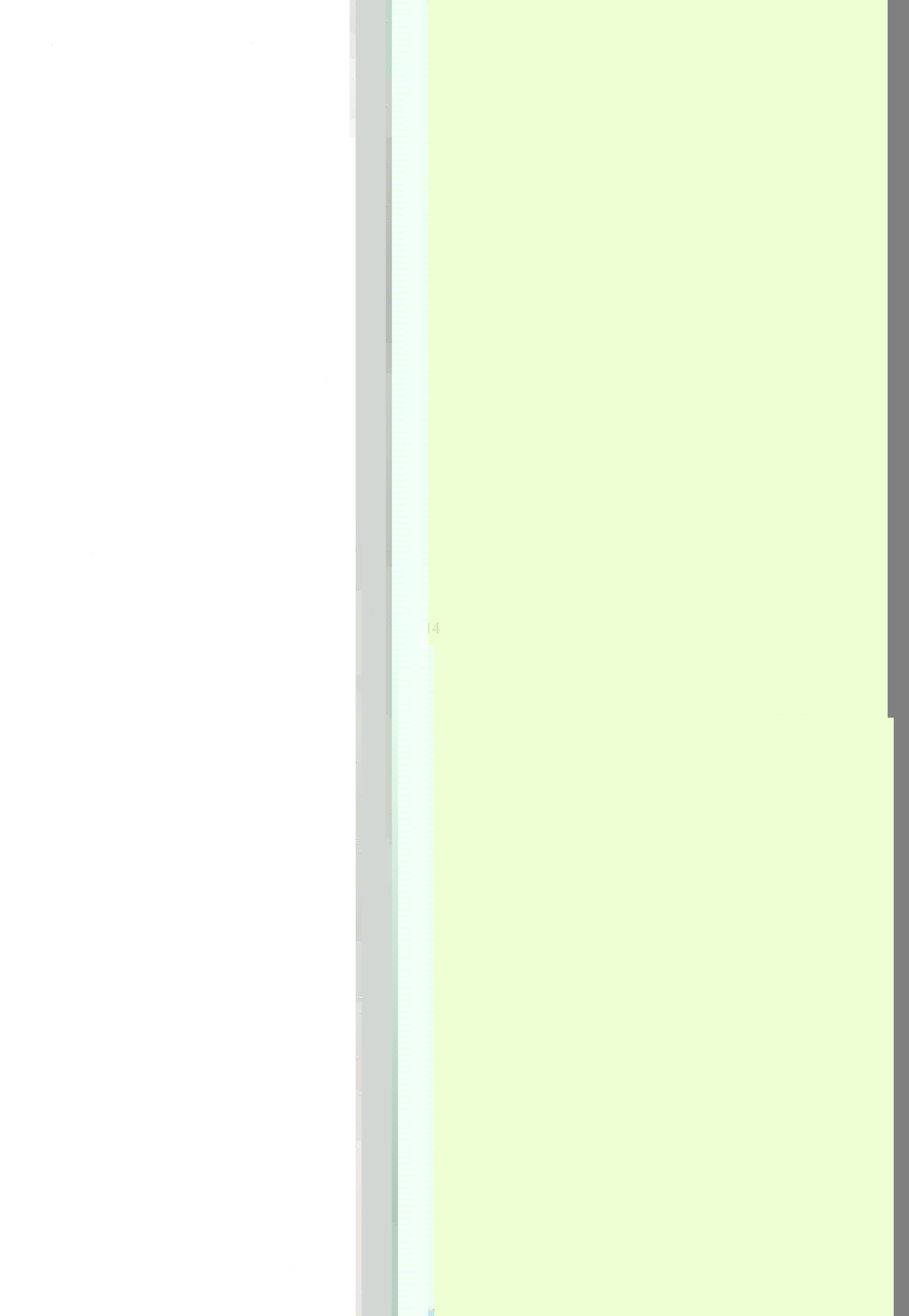

Preliminary Results on Aberration-Corrected STEM in National Taiwan University: Practical Aspects on STEM-EDX Mapping at Atomic Resolution

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The installation of the first probe-corrected facility (JEOL 2100F) in Taiwan has been accomplished towards the end of September 2009. This aberration-corrected STEM is equipped with electron energy-loss spectroscopy and energy dispersive spectroscopy (EDS). Preliminary tests on the spatial resolution of the facility have been performed using Au nanoparticles and InGaAs/InAlAs superlattices, demonstrating a spatial resolution of gently better than 1 Å. First trials on chemical mapping of atomic columns by the conjunction of STEM and EDS have also been conducted, potentially suggesting its atomic-scale resolving power. Some practical aspects towards STEM-EDS at atomic resolution will be discussed.

Dynamic transmission electron microscopy (DTEM)

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In response to a need to be able to observe dynamic phenomena in materials systems with both high spatial (~1nm) and high temporal (~10ns) resolution, a dynamic TEM (DTEM) has been developed at Lawrence Livermore National Laboratory (LLNL). The high temporal resolution is achieved in the DTEM by using a short pulse laser to create the pulse of electrons through photo-emission (here the duration of the electron pulse is approximately the same as the duration of the laser pulse). This pulse of electrons is propagated down the microscope column in the same way as in a conventional high-resolution TEM. The only difference is that the spatial resolution is limited by the electron-electron interactions in the pulse (a typical 10ns pulse contains ~10^8 electrons). To synchronize this pulse of electrons with a particular dynamic event, a second laser is used to "drive" the sample a defined time interval prior to the arrival of the laser pulse. The important aspect of this dynamic DTEM modification is that one pulse of electrons is used to form the whole image, allowing irreversible transitions and cumulative phenomena such as nucleation and growth, to be studied directly in the microscope. The use of the drive laser for fast heating of the specimen presents differences and several advantages over conventional resistive heating in-situ TEM – such as the ability to drive the sample into non-equilibrium states. So far, the drive laser has been used for in-situ processing of nanoscale materials, rapid and high temperature phase transformations, controlled thermal activation of materials and work is underway to develop the technology for imaging live biological samples (currently being implemented on a new DTEM at UC-Davis). The microscope being designed and implemented at UC-Davis will take the DTEM a step further in combined spatio-temporal resolution by incorporating aberration corrected lenses. In this presentation, a summary of the development of the existing DTEM, its current and future applications to materials/biological structures, and the potential improvements in spatial and temporal resolution that can be expected through the implementation of upgrades to the lasers, electron optics and detectors used in the DTEM will be discussed.

Aspects of this work are performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory and supported by the Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and

Engineering, of the U.S. Department of Energy under Contract DE-AC52-07NA27344. Additional aspects of this work at UC-Davis were supported by DOE NNSA-SSAA grant number DE-FG52-06NA26213 and by NIH grant number RR025032-01

Ultra-high vacuum electron microscopy and the development of Cs corrector

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The importance of ultra-high vacuum (UHV) environment has been pointed out not in surface science but in atomic scale analysis using transmission electron microscopy (TEM). However, the vacuum level in modern TEMs is still in the order of 10^{-6} Pa, which is not good enough to eliminate surface contamination. The surface structures of materials appeared in the UHV environment are also very important for semiconductor industries to control the nanostructures in atomic scale. We have developed an ultra-high vacuum field-emission TEM (UHV-FE-TEM) for the observation of semiconductor surfaces. It provides a vacuum level of 2.0 x 10^{-8} Pa, in addition to high contrast electron probe with large beam current for high-resolution transmission electron microscopy (HRTEM). Nanometric surface analysis using EDS and EELS can be carried out simultaneously with HRTEM. The UHV level at specimen surface of the microscope was proved to be demonstrated by the imaging of reconstructed 7x7 structure of Si (111) surface. Then various metals, such as Pd and Fe, were deposited on the surface to investigate the microstructural changes in atomic scale. The results indicated the importance of UHV environment for TEM analysis.

Recent successful development of TEM is of course an aberration correction of probe forming lens of scanning transmission electron microscope (STEM). Besides major advantage of the improvement of resolution down to 0.1 nm, one of serious problems of intense and focused electron beams is the contamination of specimens during observation and analysis. Ultra-high vacuum TEM (UHV-TEM) is realized as a powerful tool at this point. However, The UHV compatible Cs corrector has not been realized yet because of only a technical reason that will be the major step forward in electron microscopy. To achieving it, we are now developing an UHV-compatible Cs corrector with JEOL Ltd. for the probe forming system of our STEM (JEM-2500). The basic concept of the corrector is similar to that by M. Hider and H. Rose which consists of two stages, each one of which has 12 poles and transfer lenses. The 12 poles mainly act as a two sextuple corrector and it can also be excited as two dipoles and two quadrupoles to compensate beam shifts and stigmatisms.

After confirming a vacuum of 1×10^{-7} Pa, the beam contamination was observed for a $SrTiO_3$ TEM sample. HAADF-STEM images of the same as-thinned $SrTiO_3$ TEM sample were taken using a standard STEM (JEM-2100F) with a regular vacuum

and using the Cs-corrected STEM with the UHV environment. It is clearly observed that the contamination of the sample was greatly reduced in the UHV environment, and this result indicates the usefulness of the Cs-corrected UHV STEM.

Growth and defects dynamics in nano-sized materials studied by transmission electron

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As the size of a material decreases down to nanometer levels, the surface (free surface or interface) plays an increasing role in governing the phase (also structure and shape) stability and chemical/physical properties of material. In this talk, several case studies of in-situ transmission electron microscopy (TEM) are presented and address the surface effects on growth and deformation mechanisms of nanometer sized crystals.

An oscillatory mass transport mechanism was observed for the self-catalytic VLS growth of sapphire (α-Al_2O_3) nanowires at the atomic scale by in-situ TEM. The mass transport is accomplished via the local growth and subsequent dissolution reactions at the triple junction. The observed two-step mass transport mechanism is believed to be the one that costs the least energy barrier associated with the force balance interaction between the three interfaces intersecting at the triple junction.

Tensile straining of a wire pattern structured within 500 nm thick Al film provided a direct insight into source controlled dislocation plasticity. During the deformation single-ended sources emit dislocations that escape the crystal before multiplying. This keeps the dislocation density statistically constant throughout the deformation since nucleation and loss rates counterbalance at 0.2 events per second. On the other hand, the tensile straining of a cross-sectional Al/polyimide sample resulted in pile-up of dislocations near the passivated film surface, which shows that the surface state of crystal governs dislocation plasticity at the nanometer scale.

Meeting Feynman's challenge

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This contribution addresses advances in electron microscopy that were accomplished over the past years by the incorporation of new electron-optical components such as aberration correctors, monochromators or high brightness guns (Figure 1). Many of these developments were pursued within the DoE's TEAM project that was recently concluded (http://ncem.lbl.gov/team/TEAMpage/TEAMpage.html). As a result electron microscopy has reached 50 pm of resolution, which is now limited by the Coulomb scattering process itself and not longer by instrument performance. It is now established that the resolution improvement has helped to boost signal to noise ratios for the detection of single atoms across the Periodic Table of Elements. Consequently it became possible to identify the atomic structure of single point defects in graphene and BN and the three-dimensional location of interstitial atoms in crystals. Feynman's Challenge, " *...to make an analysis of any complicated chemical substance; all one would have to do would be to look at it and see where the atoms are....* " can now be met. New research areas such as the quest for more sustainable energy solutions largely benefit from this development since catalytic materials and polymers can be imaged time resolved at atomic resolution with single atom sensitivity.

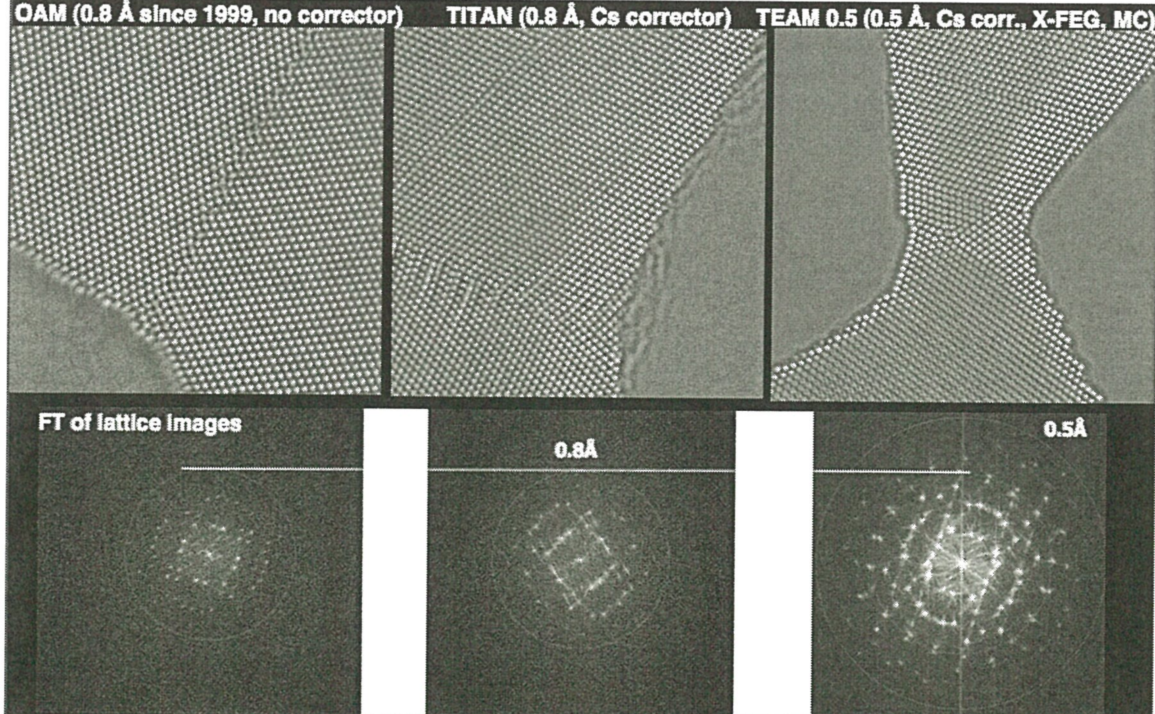

Figure 1: Progress in electron microscopy, instruments as indicated. Top: Reconstructed phase images of gold [110]. Bottom: Fourier transform of single lattice images.

50pm resolution electron microscope, performance and applications

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An R005-TEM/STEM electron microscope has been developed. The microscope has achieved sub-50pm resolution by using a new spherical aberration corrector having an asymmetric configuration, and a new 300 kV cold field-emission gun (CFEG). A new objective lens developed for the R005 microscope has a wide space for tilting, heating, and cooling our specimens, using conventional specimen holders. The resolution of the microscope, tested by observing "dumbbell image" of a germanium crystal in HAADF-STEM, gave an atomic-column resolution of 47pm, the separation of the neighboring [114] atomic columns.

The basic performance of the R005 electron microscope is high and enough for quantitative analysis of both image and chemical characteristics. The new CFEG has a stable emission intensity, which does change less than 10% after eight hours continuous observation. The energy spread is 0.4eV for usual operation (the smallest value is 0.32 eV). Although Cs correctors generally produce inevitable increase of the chromatic aberration (Cc) of the objective lens and damages the image resolution, the present asymmetric Cs corrector suppresses Cc increase. The asymmetric Cs corrector and the CFEG, thus, give a great advantage for achievement of 50pm electron microscopy. The Cs corrector provides 50mrad for the maximum Cs-correction semi-angle for the STEM incident beam. Experiment and simulation showed ~ 40pm as the STEM probe (FWHM) for 30mrad of the incident STEM beam.

The 47pm separated dumbbell images, a pair of [114] atomic columns of germanium crystal, is obtained with a 10.2 % contrast of the dumbbell image using a 0.4 eV energy spread of the incident electron beam and 30mrad for the incident beam aperture half angle. The experiment accords with the simulation by full dynamical calculation (15.6% contrast). The large aperture angle for the incident STEM probe allowed us section imaging of dopants in crystals by Z-contrast imaging with a thickness resolution of around 3nm: The dopants within a slice of 3nm thickness can be imaged. Dopants of small Z (atomic number) difference from that of the host crystal are discriminated better as the resolution increases.

In TEM images 50pm resolution showed an advantage in resolving individual atoms quantitatively. Individual carbon atoms in grapheme sheets such as vacancy, adatoms on-top site and bridge-site (atom-atom separation of 70pm) are directly

resolved in TEM images. In-situ heating, cooling, and gas-inlet systems developed (commercial specimen holders are also adaptable at R005 microscope) give some new sights about defect structures and their changes in TEM images. The developed R005-microscope with in-situ capabilities gives rich information of materials and nano-structures by qualitative microscopy.

The present work was supported by the Japan Science and Technology Agency (JST) under the CREST project.

Atomic resolution scanning transmission electron microscopy

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Atomic resolution imaging is possible in scanning transmission electron microscopy (STEM) using a number of different signals. A theoretical understanding of image formation is an important part of being able to maximize what can be achieved in interpretation and analysis of experimental data[1-4].

Z-contrast imaging has recently been put on a quantitative basis, with good agreement between theoretical simulations and experiment being demonstrated[5, 6]. Elemental mapping based on core-loss electron energy-loss spectroscopy (EELS) is also increasingly being used in tandem with Z-contrast imaging[7, 8]. A theoretical understanding of channelling and inelastic scattering processes (both phonon excitation and the core-loss process) is needed to understand and accurately interpret the images. For example, using different energy windows above the $L_{2,3}$ edge in <011> silicon to map the position of the atomic columns, we find a contrast reversal which produces an apparent and misleading translation of the silicon columns[9]. Using simulations of the imaging process, we explain the intricate physical mechanisms leading to this effect.

It is also now possible to map chemical images at the atomic scale using energy dispersive x-ray (EDX) analysis based on the x-rays emitted when core holes are filled post ionization[10]. With the advent of x-ray detectors spanning nearly 1 srad, the quality of such images will improve[11]. The inelastic cross section for EDX for a particular core-loss can be modeled as being proportional to that for an EELS experiment for the same ionization edge but for a detector spanning the whole solid angle and with an energy window which incorporates all energy losses above threshold. This insight allows us to understand why the effective optical potential for ionization is local in this case and, in addition, why contrast reversals are avoided.

L.J. Allen acknowledges support by the Australian Research Council and the essential contributions of A.J. D'Alfonso, A.L. Bleloch, M. Bosman, S.D. Findlay, B. Freitag, M.P. Oxley, V.J. Keast and P. Wang to this work.

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Processing HREM images to quantitative 3D atomic structures: Where are we?

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In the future we see an evolution from describing to understanding and even designing structures with known properties. The basis for this is the interaction between theory and experiment. The language is necessarily the language of numbers such as precise atomic coordinates. Quantitative structure information can only be obtained from HREM images if one has a model for the object and if the image contrast can be measured quantitatively [1]. The atoms constitute the "alphabet" of matter. This organization of nature provides a unique opportunity for a model-based approach to interpret the images, provided the microscope would have sufficient resolution to visualize the individual atoms.

In principle, the atom positions can be determined quantitatively by iteratively fitting the experimental image with computer simulations. If the atoms can be resolved experimentally (or using direct methods) the refinement only alters the atom positions slightly so that convergence to the optimal solution is guaranteed. The precision, that is, the standard deviation, on the atom positions that can thus be reached can be adequately quantified in the form of a lower bound s on the standard deviation [2]. It can be shown that s depends on both the Rayleigh-like resolution ρ and the available dose of imaging particles N, according to the formula $s \sim \rho/\sqrt{N}$. This procedure is comparable to X-ray crystallography where one first tries to "resolve" the atomic structure of a crystal using so called "direct methods" and afterwards refines the structure iteratively.

However, a big problem arises if the interatomic distances are smaller than the resolution. Then, the images of most neighboring atoms overlap so that the individual atoms are not resolved. In that case one cannot find a reasonable trial structure to start the refinement. Due to the strong overlap of the neighboring atoms, the influence of all the coordinates is in a sense coupled in the image. One cannot alter one coordinate without affecting the others. Finding the optimal fit then becomes an optimization problem with many strongly correlated parameters. This introduces severe problems of computational kind. Computational problems can only be overcome if the individual atoms in projection are discriminated, The most challenging structures in this respect are amorphous materials where individual atoms in projection can only be resolved if the thickness is very small., i.e for a resolution of 0.1 nm, the maximal foil thickness is limited to about 2 nm, which is unrealistically small. Improving the resolution either by deblurring the microscope with holographic reconstruction methods or by reducing the C_s value will not cure the problem. Indeed, even in a

"perfect" electron microscope the image of an atom will reveal its projected electrostatic potential, which has an intrinsic "width", which for silicon is already of the order of 0.1 nm. This is the intrinsic resolution of the object. This is the reason why an amorphous silicon object cannot be used to determine the resolution of a microscope below 0.1 nm.

In order to resolve and refine amorphous objects one has to use electron tomography, which allows one to resolve the 3D amorphous structure so that individual atoms can be discriminated. Furthermore, the number of images (dataplanes) is much larger, whereas the number of atom coordinates increases only from 2 to 3. In that case, it can be shown that a microscope resolution of 0.2 nm is sufficient to resolve and refine amorphous structures.

Another important problem is that at the high accelerating voltages used for atomic resolution TEM (200-300 keV) the amorphous structure is continuously damaged by the electron beam. It is to be believed that much lower voltages are needed for reliable quantitative studies. However, lowering the voltage also deteriorates the instrumental resolution. In order to keep the resolution at that voltage close to the intrinsic object resolution of 0.1 nm one will need to correct both spherical and chromatic aberration by using a spherical aberration corrector and a monochromator. As shown in figure 1, these corrections improve the precision as well. The lower bound s on the standard deviation of the position of a single projected atom is evaluated as a function of C_s, for an energy spread of 0.72 eV (monochromator off) and 0.02 eV (monochromator on), assuming a 50 keV accelerating voltage. At each setting, the recording time is kept constant, assuming that specimen drift puts a practical limit to the experiment. From this figure, it is clear that the precision is highest, that is, the standard deviation is lowest, when using both a C_s corrector and a monochromator. Moreover, this figure shows that, in the absence of a monochromator, the precision decreases if C_s is corrected. It can thus be concluded that, at the low accelerating voltages, which are needed for the study of amorphous objects, a C_s corrector combined with a monochromator is needed in order to resolve and refine the structure.

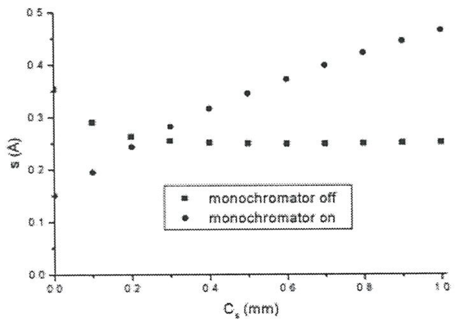

Fig. 1: Lower bound s on standard deviation of a single Si atom position as a function of C_s, for an energy spread of 0.72 eV (monochromator off) and 0.02 eV (monochromator on), assuming a 50 keV accelerating voltage. At each setting, the recording time is kept constant

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Structural studies of nanoparticles in two and three dimensions using aberration corrected electron microscopy

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Electron optical aberration correction in both TEM and STEM geometries is now a firmly established[1, 2] technology with a variety of imaging and probe corrected instruments installed at many laboratories around the world. In parallel, the alternative, complementary approach to direct correction, involving computational compensation of measured coefficients of the wave aberration function, a posteriori during exit wave reconstruction from series of images recorded with different focus values[3] or with different illumination tilts[4] is widely used to improve the quantification of TEM data. More recently these two approaches have been successfully combined for both focal[5] and tilt series geometries[6].

In this paper we will describe the combined use of electron optical aberration correction and exit wave reconstruction in studies of metal and metal oxide nanoparticles with particular reference to the structure and composition of catalytically active surfaces. We will show how it is possible to determine local surface structures for metal particles in projection and to characterise surface terminations in metal oxide nanoparticles. In both cases, the experimental data obtained will be compared to large scale thermodynamic calculations of the appropriate phase diagrams in order to gain insight into the relationship between surface structure and particle morphology as a function of catalytically relevant parameters.

Electron optical aberration correction also gives rise to a narrow depth of field and offers the intriguing possibility of depth sectioning of samples in similar fashion to confocal scanning optical microscopy (CSOM). This approach denoted Scanning Confocal Electron Microscopy (SCEM) potentially provides an alternative to tomography for providing 3D information from laterally extended objects in an efficient fashion. We will describe initial results from this mode using both inelastic scattering (EFSCEM) and annular dark field imaging (ADF-SCEM) of nanometer sized catalyst particles.

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Atomic imaging and interpretation using secondary electrons and transmitted electrons with an aberration corrected scanning electron microscope

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We report the simultaneous acquisition of atomic images using secondary (SEM) and transmitted (STEM) electrons to achieve unprecedented spatial resolution for periodic crystal lattices and isolated single atoms. The instrument is the first Hitachi aberration corrected scanning electron microscope, HD2700C, recently installed at BNL. It has a cold-field-emission electron source, a CEOS probe corrector, an Enfiner spectrometer, and five detectors including one that collects secondary and back scattered electrons emerging from the top surface of the sample[1]. Bias experiments reveal that these surface sensitive electrons are dominantly secondary electrons, which were believed not possible to give atomic resolution due to the delocalization[2]. Quantitative analysis of the image intensity of several hundreds of individual atoms, using the corresponding STEM/ADF images as a reference, suggests the signal does not have any tails, implying the generation of the secondary electrons can be attributed to the large-momentum-transfer single-electron inelastic scattering events, rather than the decay of collective electronic excitation as previously assumed. The ability to image surface and bulk structure simultaneously at atomic resolution can revolutionize the field of microscopy and imaging.

Although aberration correction improves spatial resolution, it does not make image interpretation easier due to the large convergent angles used to gain beam current. To understand STEM/ADF image contrast, we developed our own computer codes based on the multislice method with frozen phonon approximation to calculate ADF images and compare them with experiment. Our study demonstrates that the ADF image contrast (or Z-contrast) does not follow the simple $I \sim Z^2$ or $I \sim Z^{1.8}$ power rule as many expect. ADF images indeed show Z-dependence contrast, however, the power law is only valid under very high collection angles for very thin specimen. The ADF image intensity also strongly depends on dynamic and static lattice displacement of the sample. To correctly interpret the ADF images, the effect of atomic thermal vibration (Debye-Waller factor) of the atoms must be taken into account[3].

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Electron Diffractive Imaging at Sub-Å Resolution

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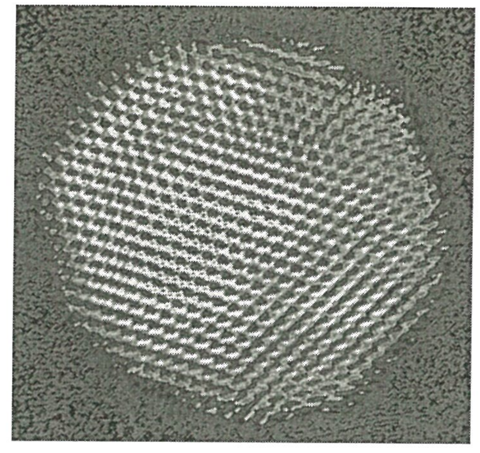

Nanoscience and nanotechnology is about controlling, manipulating and interfacing different structures that are few to hundreds nanometers in size. The properties of these nanostructures are heavily influenced by their structure and their surfaces. Determination of the atomistic structure of nanostructures is still an unmet challenge despite of tremendous progresses that have been made in nanoscale characterization techniques, including aberration corrected transmission electron microscopy. A major obstacle is how to obtain 3D structure information under beam damage thresholds. Electron diffractive imaging is a promising approach. Recent studies have shown coherent electron diffraction patterns can be recorded from individual nanostructures using medium energy electrons (10 to 200 kV).[1,2,3] The amplitudes recorded in a diffraction pattern are unperturbed by lens aberrations, defocus and other microscope resolution limiting factors. Sub-Ångstrom signals are available beyond the information limit of direct imaging. Here we report the realization of sub-Å electron diffractive imaging and demonstrate the potential of this new imaging technique by using nanometer-sized CdS quantum dots (see figure above)[4] and carbon nanotubes as examples. The solution of the phase problem is achieved using an iterative phase retrieval algorithm. The diffraction patterns were recorded from individual quantum dots using a nanometer-sized, coherent and parallel, electron beam. Complex wavefunctions are reconstructed from the diffraction intensities. Atoms at sub-angstrom distances are resolved. Significant contrast improvement is obtained compared to high resolution electron micrographs. The issues critical to reconstruction will be discussed in the talk; these include missing information in recorded electron diffraction patterns, the robustness of the reconstruction algorithms in the presence of experimental noises, the object support and its effect on reconstruction. Progress towards 3D imaging will be discussed.

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Three-dimensional electron CDI of a nanocrystal

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Electron coherent diffractive imaging (CDI) is a promising technique for investigating the structure of nanoparticles down to the atomic scale. Up to now, a two-dimensional electron CDI has been demonstrated [1]. Here, for the first time, we have experimentally determined a three-dimensional (3D) morphology of an individual nanocrystal using electron CDI in the Bragg geometry. In the experiment, we used a common electron microscope (JEOL 2010F) equipped with a field-emission gun, which produce a highly coherent nano-sized illumination. In our data analysis, we have developed a guided algorithm with a dynamic support, which provides an optimal solution deduced from the electron diffraction pattern alone. The result of the reconstruction shows that the recorded continuous 3D diffraction pattern around the (020) reflection of the MgO nanoparticle reveals the 3D shape of the sample consistent with simulation. The angular measuring range of only 1.7° provides a spatial resolution of a few nanometers along direction of the electron beam propagation. In comparison with conventional electron tomography, proposed method enables determination of 3D morphology of nanocrystals without the use of a dedicated tomography sample holder. We believe this experiment provides a first step toward the 3D electron CDI at atomic resolution.

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研究室簡介

本研究室自成立以來，積極從事工業材料及製程之檢測分析技術開發及工業服務，並致力於各類材質微區分析技術、材料表面及界面分析技術、界面及微結構對材質特性影響之研究等。

核心技術

*微結構分析技術

電子顯微鏡(SEM、TEM、 HRTEM、3D Tomography)
聚焦離子束儀(DB-FIB)、先進定點樣品製備技術
X光繞射儀(XRD) 等相關分析技術

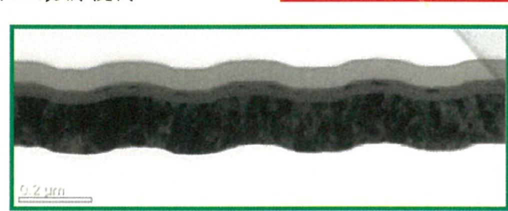
*表面分析技術

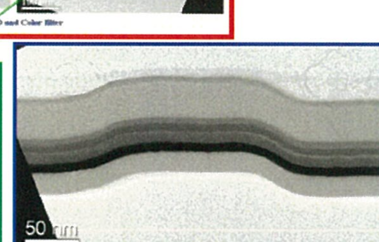
掃描式歐傑電子顯微鏡(AES)
化學分析電子儀(ESCA/XPS)
原子力顯微鏡(AFM) 相關分析技術

*化學分析技術

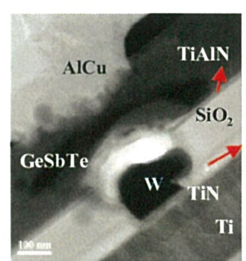
感應耦合電漿質譜儀 (ICP-MS)
原子吸收光譜儀(AAS)
拉曼分析(μ-Raman) 等相關分析技術

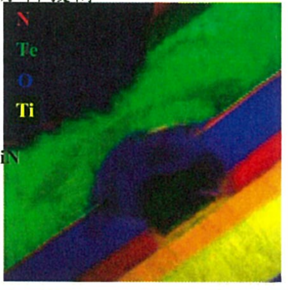
MCL
Layer thickness measurement and interface observation
Al electrode 135nm
organic layer 360nm
organic layer
ITO 215nm
Color filter
A 3.9nm interlayer between ITO and Color filter



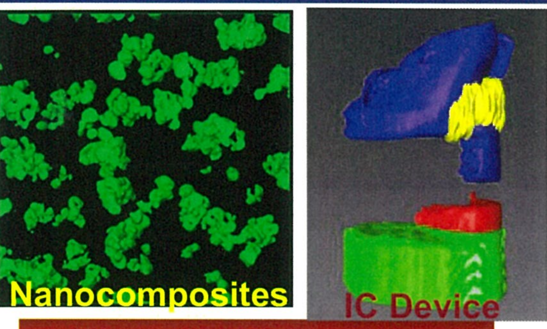


商用有機發光元件與儲存媒體之膜層厚度與成分分析





EELS mapping analysis of IC device



TEM 3D Tomography結構分析

Nano-Structure

SEM image

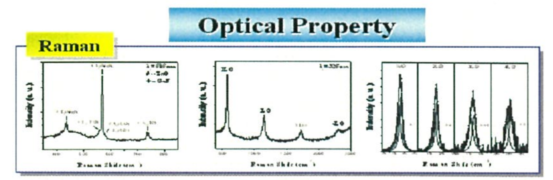
直接使用氧化鋅緩衝層能有效成長高密度（~10^{10} cm^{-2}）垂直氧化鋅奈米線於矽基版上，奈米線的平均長度約2.8~3.0 μm，線徑 約 80~100 nm。

TEM image

高解析穿透式電子顯微鏡影像證實氧化鋅奈米線為高品質單晶結構，並長軸延(0002) 方向成長。

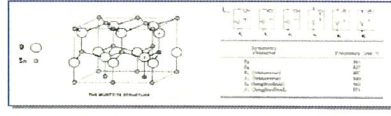
Optical Property

Raman

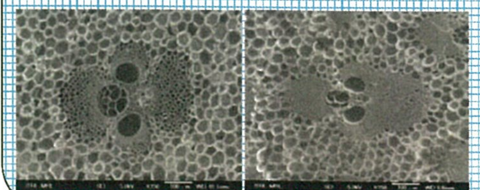


利用 UV Raman 散射，觀測到在氧化鋅奈米線的聲子共振態，*A1*(nLO)/*E1*(nLO)的強度比例，隨 n 值增加有升高的趨勢，那是由於隨線徑的縮小，延a軸方向振動的*E1*(nLO)強度遞減的比延c軸方向振動的*A1*(nLO)要來得快，此現象證實了奈米線的聲子振動有明顯的量子侷限效應。

氧化鋅聲子振動模型



竹炭-電子顯微鏡微觀結構圖



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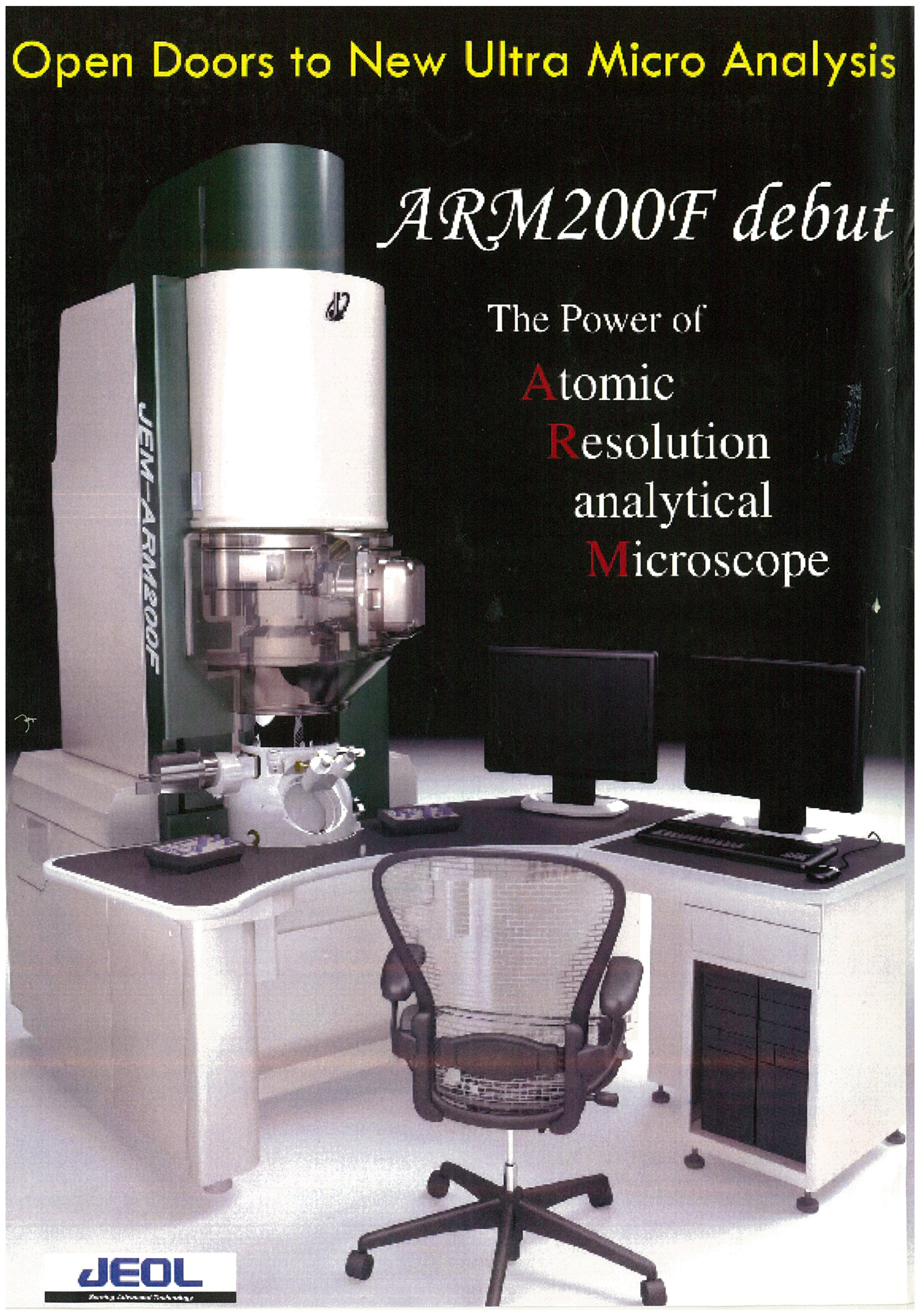

Open Doors to New Ultra Micro Analysis
ARM200F debut
The Power of
Atomic
Resolution
analytical
Microscope
JEM-ARM200F
JEOL